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Facile synthesis of monodisperse ZnS capped CdS nanocrystals exhibiting efficient blue emission

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Abstract A new method for the capping of colloidal CdS nanocrystals with ZnS shells is presented. A combination of the monomolecular precursor zinc ethylxanthate ($\text{Zn}(\text{ex})_2$) and zinc stearate was used to replace hazardous organometallic reagents usually applied in this procedure, i.e. bis(trimethylsilyl) sulfide and diethylzinc. Its simple preparation, air-stability and low decomposition temperature of 150 °C make $\text{Zn}(\text{ex})_2$ a very suitable source for the ZnS shell growth. With this precursor, highly luminescent CdS/ZnS core/shell nanocrystals (Q.Y. 35–45%), exhibiting narrow emission linewidths of 15–18 nm (FWHM) in the blue spectral region, can reproducibly be obtained.

Keywords Semiconductor nanocrystals · CdS · ZnS · Fluorescence · Blue emission

Introduction

Since the discovery of the quantum confinement effect [1], colloidal semiconductor nanocrystals have been intensively studied due to their unique size-dependent physical properties. In particular cadmium based systems (CdSe, CdTe, CdS) have drawn much attention as a consequence of the development of

several powerful synthetic methods for the preparation of monodisperse samples. The original organometallic synthesis [2] with pyrophoric dimethylcadmium as the metal precursor has found interesting alternatives in more recent preparation methods based on cadmium alkylphosphonates or cadmium carboxylates [3], often referred in literature as “green-chemical” syntheses. The capping of nanocrystals with another semiconductor is a well-established method for the enhancement of the emission efficiency in type I core/shell systems (CdSe/ZnS, CdSe/ZnSe, CdSe/CdS) [4] or for the spectral shift of the emission peak to the near infrared region in type II core/shell systems (CdTe/CdSe, CdSe/ZnTe) [5]. In the former case, zinc sulfide is the most important shell material as, due to its large band gap, both photo-generated electrons and holes are efficiently confined in the nanocrystals’ core. This is especially important when subsequent functionalization by ligand exchange is performed. Taking the examples of CdSe/CdS or CdSe/ZnSe nanocrystals: with initial surface ligands they can show high fluorescence quantum yields in the range of 50–85% [4c, d] however frequently the emission efficiency drastically decreases upon surface functionalization. Despite of the importance of the ZnS capping, no green-chemistry preparation method has been developed in this case. Mostly, the original procedure, with pyrophoric diethylzinc and highly toxic bis(trimethylsilyl) sulfide as precursors, is applied. In this communication we describe a new method in which these reagents are replaced by a monomolecular precursor, zinc ethylxanthate ($\text{Zn}(\text{ex})_2$). As in this compound the Zn/S ratio is 1:4, zinc stearate is added in order to compensate the missing quantity of zinc precursor. The presented procedure yields strongly blue

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luminescent, monodisperse CdS/ZnS core/shell nanocrystals of high color purity.

Experimental

Preparation of Zn(ex)₂

An analogous procedure to that reported for the preparation of cadmium ethylxanthate was used [6]. A solution of zinc chloride (0.005 mol in 20 ml of distilled water) was mixed with a solution of potassium ethyl xanthogenate (1.6 g (0.01 mol), in 20 ml of distilled water) under constant stirring. The resulting white precipitate was filtered, washed with distilled water and dried in vacuum. Yield 1.15 g (75%). Elemental analysis (%), experimental (calculated): Zn, 22.89 (21.11); S, 43.04 (41.40); C, 23.15 (23.26); H, 3.10 (3.90).

Preparation of CdS/ZnS nanocrystals

(1) Synthesis of 4 nm CdS nanocrystals

One millimole of cadmium stearate, 2 mmol of stearic acid, 4 mmol of oleylamine and 13.4 g of octadecene were mixed in a three-neck flask equipped with a condenser and heated under argon to 300 °C. Then 1.25 ml of a solution of sulfur in octadecene (0.08 M) was swiftly injected. The temperature was allowed to decrease to 250 °C and kept at this value for 20 min. After cooling to room temperature, 1 ml of trioctylphosphine (TOP) was added and the nanocrystals were precipitated with 10 ml of a CHCl₃/CH₃OH (1:1) mixture and 30 ml of acetone. The supernatant was discarded and the nanocrystals were redispersed in hexane. Purification was carried out by repeating this precipitation/centrifugation/redispersion cycle.

(2) ZnS shell growth

0.143 micromole of the CdS nanocrystals (quantity determined on the basis of absorbance measurements, cf. Ref. [7]) were dispersed in 5 ml of octadecene and 5 ml of oleylamine. After degassing, a mixture constituted of 0.1325 mmol of Zn(ex)₂, dissolved in 1.3 g of dioctylamine (DOA), and 0.4 mmol of zinc stearate in 5 ml of octadecene was added within 45 min by means of a syringe pump. Aliquots were taken during the injection to monitor the shell growth. The purification was carried out in the same way as for the core nanocrystals without adding TOP.

Characterization techniques

Solution UV–vis spectra were recorded on a HP 8452A spectrometer (wavelength range 190–820 nm). Photoluminescence measurements were carried out with an AvaSpec-2048-2 spectrofluorometer using a blue LED (400 nm) for excitation. EDX analyses were performed with a JEOL JSM-840A scanning electron microscope equipped with an Oxford Instruments energy dispersive X-ray analyzer and TEM images were obtained with a JEOL 4000EX transmission electron microscope operated at 300 kV. Elemental analysis of Zn(ex)₂ was carried out by the Analytical Service of CNRS Vernaison (France). A thermo balance SETARAM TG 92-12 was used for thermogravimetric analysis applying a heating rate of 10 K/min under air. Powder X-ray diffraction was performed with a Philips X'Pert MPD diffractometer using a Co X-ray source operated at 50 kV and 35 mA with a secondary graphite monochromator.

For the determination of the room temperature fluorescence quantum yield (Q.Y.), the spectrally integrated emission of a CdS/ZnS nanocrystal dispersion in hexanes was compared to the emission of an ethanol solution of coumarine (Q.Y. = 73%) of identical optical density at the excitation wavelength (400 nm). Mean values of the Q.Y. were established by repeating the measurements for different dilutions.

Results

CdS nanocrystals were prepared according to the method published by Yu and Peng [8] using an oleylamine/octadecene solvent mixture instead of pure octadecene. In our experiments, the addition of a primary amine to the solvent led to a narrowing of the size dispersion, indicating that amine molecules, by interacting with cadmium ions, can influence the crystal growth kinetics. A similar behavior has been observed in the case of CdSe nanocrystals' synthesis in coordinating solvents [4d, 9]. After the synthesis, we attempted to purify the CdS nanocrystals by standard cycles of precipitation with a polar solvent or a solvent mixture and redispersion in a non-polar solvent. We found, however, that, by this method, octadecene and non-bound stearic acid molecules are difficult to separate from the CdS nanocrystals complexed with initial surface ligands due to similar solubility parameters. The purification is considerably facilitated by addition of a small amount of TOP to the crude reaction mixture. TOP can bind to the nanocrystals' surface and complete in this way the ligand shell consisting of

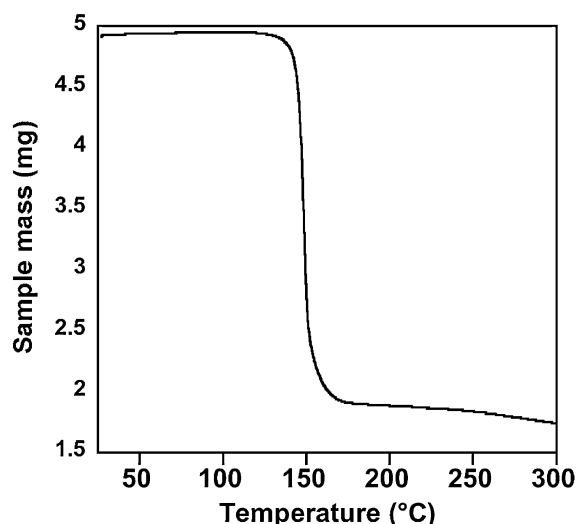


Fig. 1 Thermogravimetric analysis of $\text{Zn}(\text{ex})_2$

stearic acid. Furthermore the alkyl chains of TOP are much shorter than those of octadecene or stearic acid, reducing possible hydrophobic interactions between the nanocrystals' surface and the hydrophobic components of the reaction medium.

In the subsequent ZnS shell growth we have decided to use $\text{Zn}(\text{ex})_2$. To serve as a precursor for ZnS shell growth, $\text{Zn}(\text{ex})_2$ must decompose at temperatures lower than those used for the core nanocrystals' synthesis, ideally lower than 200 °C. As seen from the thermogravimetric analysis, this is the case. Figure 1 shows the thermogravimetric curve of $\text{Zn}(\text{ex})_2$, which reveals a distinct weight loss at 149 °C corresponding to 61% of the initial mass, leading to a residual of the hypothetical formula ZnS_2 .

The concentration of the CdS nanocrystals used for the ZnS shell growth was determined by means of UV–vis absorption spectroscopy [7] and the quantity of $\text{Zn}(\text{ex})_2$ necessary for five ZnS monolayers was slowly added to the core nanocrystal dispersion at 225 °C. As in the $\text{Zn}(\text{ex})_2$ molecule the Zn/S ratio is 1:4, the calculation of the needed precursor quantity (cf. Ref. [10]) is based on sulfur and the missing quantity of zinc

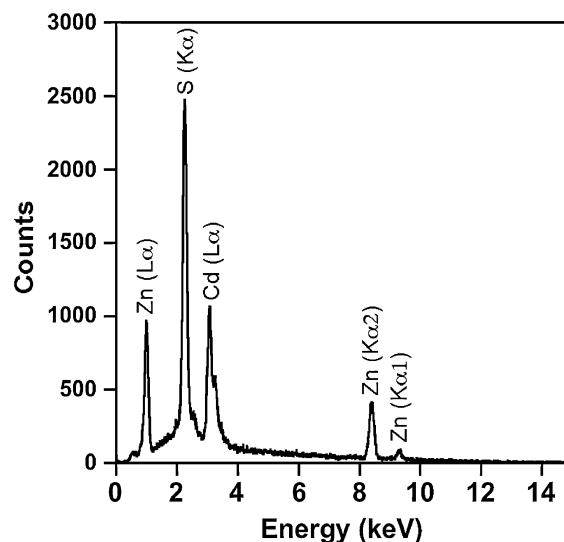


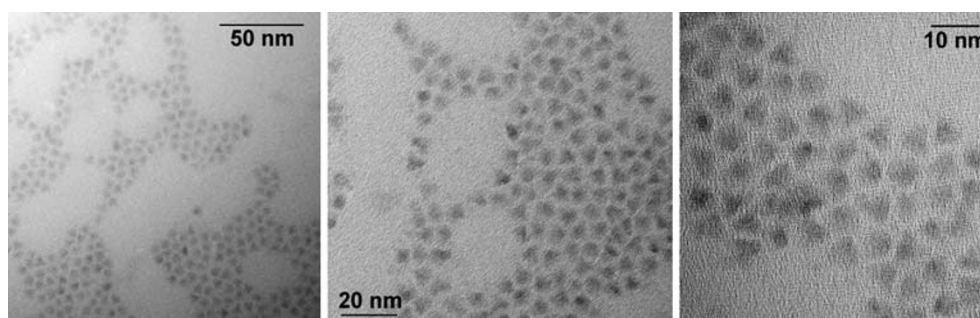
Fig. 3 EDX analysis of the prepared CdS/ZnS nanocrystals

precursor is compensated by zinc stearate. The latter compound acts also as the source of stabilizing stearate ligands for the nanocrystals' surface.

Figure 2 presents TEM images at different magnifications of the prepared CdS/ZnS nanocrystals. In contrast to the used spherical 4 nm CdS core nanocrystals, the core/shell particles exhibit predominantly a tetrahedral shape with an edge length of 6.8 nm. They are nearly monodisperse and arrange themselves into 2D networks. Due to the low contrast of ZnS it is difficult to exactly determine the nanocrystals' size and in particular the shell thickness. EDX analysis providing S/Cd/Zn atomic ratios is helpful in this respect (Fig. 3).

The ratios found were 53.4% S, 28.6% Zn and 18.0% Cd. The Zn/Cd ratio of 1.59:1 is in a very good agreement with the calculated ratio necessary for the formation of 5 ZnS monolayers on 4 nm CdS nanocrystals. Therefore it can be concluded that the process of the shell formation is essentially quantitative. Figure 4 shows the X-ray diffractogram of the same sample. The comparison of the corresponding

Fig. 2 TEM images at different magnifications of the prepared CdS/ZnS nanocrystals



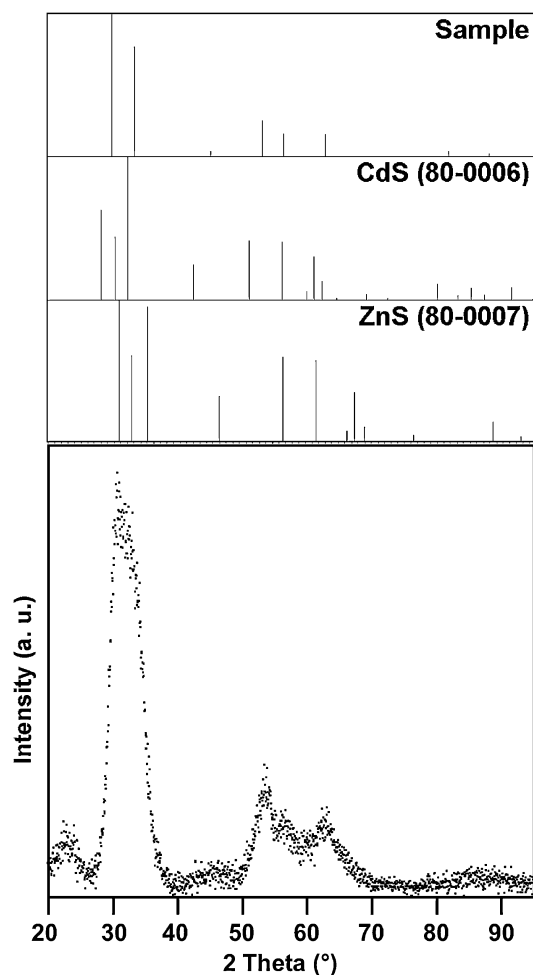


Fig. 4 Bottom: Powder X-ray diffractogram of the CdS/ZnS nanocrystals. Top: XRD patterns of the sample, of wurtzite CdS (JCPDS file 80-0006) and of wurtzite ZnS (80-0007)

diffraction patterns exhibits that the reflection angles lie between those characteristic of pure wurtzite CdS and those of pure wurtzite ZnS, which is expected for the CdS/ZnS core/shell system.

Figure 5 shows the evolution of the absorption and emission spectra of the nanocrystals during the growth of the ZnS shell. In the UV–vis absorption spectra the pronounced excitonic peak as well as several higher energy absorption features indicate a stable narrow size distribution throughout the entire reaction time. This is confirmed by the corresponding PL spectra (Fig. 5b). The photoluminescence of the CdS core nanocrystals is dominated by deep-trap emission spanning over the whole visible range. This broad emission is nearly completely suppressed even for small amounts of the injected ZnS precursor. During the first stage of the addition, the PL peak undergoes a bathochromic shift from 442 to 463 nm and then its position stabilizes. This shift, attributed

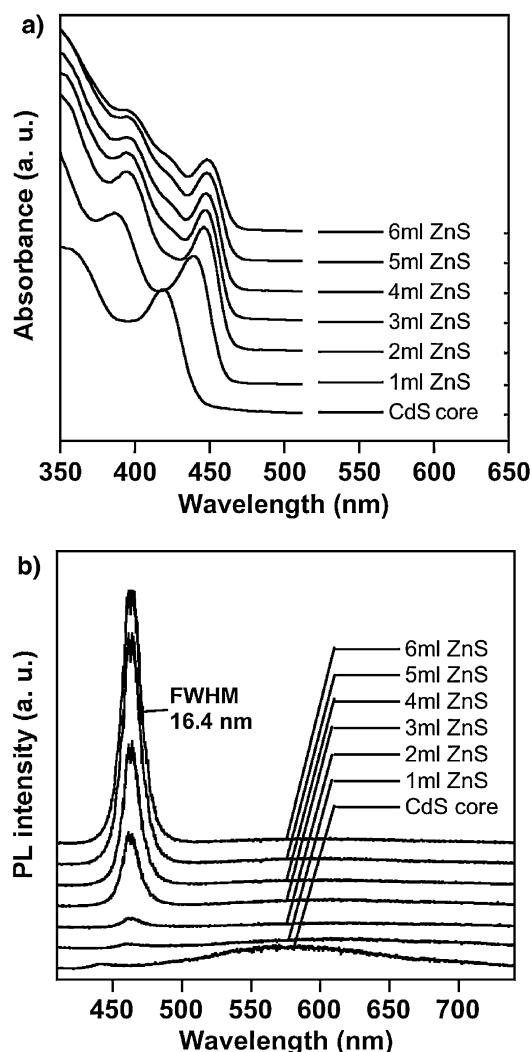


Fig. 5 (a) UV–vis absorption spectra; (b) PL spectra (excitation wavelength 400 nm) recorded during the addition of 6 ml of the ZnS precursor solution. This corresponds to the growth of a ca. 5 monolayer thick ZnS shell on the 4 nm CdS core nanocrystals. The spectra are shifted vertically for clarity

to partial leakage of the excitons into the shell, is similar to that reported for CdS/ZnS nanocrystals prepared by other synthetic routes [11]. Remarkably, the PL peak linewidth does not broaden throughout the growth of 5 ZnS monolayers and is as narrow as 16.4 nm (FWHM). This behavior is significantly different from that reported for other preparation methods where the linewidth of the CdS cores (ca. 17–19 nm) usually increases to values of ca. 24–26 nm upon the growth of 2–3 ZnS monolayers [11]. The fluorescence quantum yield of the discussed sample is 41% ($\pm 5\%$). Similar values have been measured for other samples studied, emitting in the spectral region of 440–480 nm.

Discussion

The growth of ZnS shells on CdSe nanocrystals, reported for the first time one decade ago, [4] has led to a huge amount of synthesis work devoted to core/shell systems. The precursors used for the shell growth have to fulfill several requirements. First, they have to be soluble in an organic solvent to enable a slow injection into the reaction mixture, which, in turn facilitates a homogeneous shell growth and prevents from the nucleation of the shell material nanocrystals. Second, the temperature of ZnS formation has to be sufficiently low, typically inferior to 230 °C, so that ripening of the core nanocrystals leading to spectral broadening of the emission peak can be minimized. In addition, precursors suitable for the industrialization of the nanocrystals' preparation procedure must be safe, air-stable, easy to handle and, if possible, commercially available at low cost.

Following these criteria, pyrophoric diethylzinc, initially used as the zinc source, has been replaced by zinc stearate in the preparation of ZnSe and CdSe/ZnSe nanocrystals [4d, 12, 13b]. However, the substitution of the originally used sulfur precursor (bis(trimethylsilyl)sulfide, (TMS)₂S) with an appropriate precursor has turned out more difficult. Contrary to the case of elemental selenium, elemental sulfur, dissolved in TOP, is not sufficiently reactive due to strong phosphorous–sulfur interactions. Several methods for the preparation of transition metal sulfide nanocrystals, including ZnS, with octadecene as the solvent for sulfur, have been described in the literature [13]. However, reaction temperatures in the range of 320–340 °C are necessary, incompatible with the ZnS shell growth on core nanocrystals.

More recently the use of metal alkylxanthates as monomolecular precursors for the growth of CdS [14] and Cd_{1-x}Zn_xS nanocrystals has been reported [15]. Xanthates contain both the metal and the sulfur precursors in one molecule and the metal sulfide is formed during their thermal decomposition.

Zn(ex)₂ is particularly interesting as a potential new monomolecular precursor because of its facile preparation. It can be obtained in good yields in a one-step reaction between two commercial reagents (zinc chloride and potassium ethyl xanthogenate) in water. Since it readily precipitates from the reaction medium, it can be easily purified by simple washing. Zn(ex)₂ is soluble in Lewis bases such as alkyl amines or alkyl phosphines. In this communication we have used either DOA or TOP, as the solvent for Zn(ex)₂. The evolution of the optical spectra during the shell growth is very similar in both cases and the

observed emission linewidths and fluorescence quantum yields represent the best values reported to date. The new shell growth method can easily be extended to the preparation of other core/shell and core/shell/shell systems such as CdSe/ZnS, CdSe/ZnSe/ZnS or CdSe/CdS/ZnS nanocrystals. This work is in progress.

Conclusion

We presented a new method for the overcoating of CdS nanocrystals with a ZnS shell using a monomolecular precursor, namely zinc ethylxanthate. The rather low temperature of its thermal decomposition together with its facile preparation and handling make this compound a very promising precursor for the ZnS shell growth. The obtained CdS/ZnS nanocrystals exhibit fluorescence quantum yields of 35–45%, which are the highest values observed to date for this system. Due to their narrow emission linewidths of 15–18 nm (FWHM) in a wavelength range of 440–480 nm, the prepared nanocrystals have a high potential for applications in blue emitting electroluminescent diodes and for the generation of white light when combined with green and red emitters.

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